

Immobilization of Ligands on Surfactant Coated Alumina for Removal of Cations

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ABSTRACT: In this research new adsorbents were prepared by modification of surfactant-coated γ -alumina with three ligands; 1-(2-pyridylazo)-2-naphtol (PAN), dithizone (HDZ) and dimethyl glyoxime (DMG). The adsorbents were used for removal and pre-concentration of Pb^{+2} , Cd^{+2} , Ni^{+2} , Cu^{+2} , Co^{+2} . Aqueous solutions of the metal ions were passed through a column filled with the adsorbent and the retained cations were eluted with nitric acid. Recoveries greater than 96% were obtained for most studied cations. The selectivity of the adsorbent was examined in the presence of different interfering cations. The results showed that the synthesized adsorbents possess good capacity and selectivity for the most studied cations. The reusability test of the adsorbent showed its capability after five adsorption–elution cycles.

KEY WORDS: Pre-concentration, γ -alumina, Surfactant-coated alumina, Ligand modification.

INTRODUCTION

Surfactants can form aggregates on the solid surfaces of some compounds such as silica and alumina. The hydrocarbon cores of the surfactant solubilize many hydrophobic compounds in aqueous solutions. On the other hand, typical chelating agents, such as dithizone and 1-(2-pyridylazo-2-naphtol) PAN can be incorporated into the inner hydrophobic part of the surfactant. The ligand-impregnated admicelles can be used for separation of cations. Beside the selectivity, after the cations are removed, the adsorbents can be separated by a simple filtration method. It is also possible to use them in column operation through solid phase extraction method.

Recently intensive researches have been done for preparation of new selective adsorbents by incorporation

of ligands into the solid surface of different materials. Rajesh N. used modified alumina for removal of cations by solid phase extraction method [1]. Dadfarnia used immobilized 1,5 diphencycarbazone for pre-concentration of mercury (II)[5]. Removal of some heavy metal cations by dithizone-impregnated admicelles was reported by Hiraide *et al.* [6]. Alumina supported adsorbent was used by Salavati *et al.* for removal of Mn, Co and Ni, appreciable capacity and selectivity has been reported [7]. Zaporozhets *et al.* used silica gel loaded with dithizone for determination of Ag, Hg, and Pb [10]. Manzoori *et al.* used an adsorbent prepared by immobilization of dithizone on the surfactant-coated alumina for pre-concentration and determination of mercury by cold vapor atomic

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absorption spectrometry [11]. Separation of copper by alumina and admicelar sorbents has been reported by Hiraide [12]. Two general methods are available for pre-concentration of cations. In the first method the reactant is added to cation solution to obtain insoluble complex. The complex is passed through a column containing surfactant-coated alumina for adsorption. In the second way, the ligand is immobilized on the surface of surfactant coated alumina and the cation is passed through the column containing the adsorbent. the complex is then formed on the surface of the adsorbent [8,11]. In this research, selective adsorbents were prepared by immobilization of sodium dodecyl sulfate on the surface of γ -alumina. Two ligands dithizone (HDZ) and dimethyl glyoxime (DMG) were then separately immobilized on the surface of the surfactant-modified alumina. The adsorbent were used for removal and pre-concentration of the studied cations under different experimental conditions.

EXPERIMENTAL SECTION

Immobilization of dithizone on SDS-coated alumina

15.0 mg of dithizone and 1.0 g of sodium dodecyl sulfate were placed in 50mL of 0.1M ammonia solution and diluted to 100mL with deionized water. 1.5 g of γ -alumina was ultrasonically washed in 5M nitric acid for 3min and thoroughly rinsed with water. 40mL of deionized water was added to the washed alumina and 10mL of dithizone-SDS solution was also added. The suspension was acidified to pH=2 with hydrochloric acid and was shaken for 15min before being transferred to a millipore filter holder for preparation of the column with 15mm inner diameter and 9mm height.

Immobilization of PAN on SDS-coated alumina

The reagent solution was prepared by dissolving 0.25g of PAN [1-(2-pyridylazo)-2-naphthol] in 100mL of 95% ethanol (solution A). Two grams of γ -alumina was added to 75mL of water containing 100mg of SDS and the solution was magnetically stirred. Solution A was added to the mixture and the pH was adjusted to 2.5 with hydrochloric acid. The suspension was stirred for 15min and transferred to millipore filter holder for preparation of the column.

Immobilization of DMG on SDS-coated alumina

1.0gr of DMG was dissolved in 100mL of 95% ethanol. 16mL of the solution was added to 40mL of

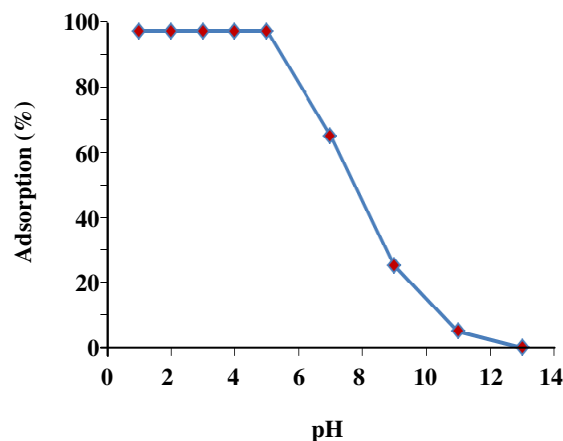


Fig. 1: Absorption of SDS on γ -alumina surface at different pH.

the mixture containing 1.5g γ -alumina. While shaking the suspension with a mechanical shaker, the pH was adjusted to 6.0 with hydrochloric acid. After mixing for 15min, the solid was separated, washed and packed into the column.

Characterization of the adsorbents

Characterization of the adsorbents was performed by Fourier Transform InfraRed (FT-IR) spectroscopy using a Nicolet Model Impact 400D and thermo-gravimetric and differential thermo-gravimetric methods by use of a thermal analyzer Mettler Model TG 50.

Adsorption of cations by modified adsorbents

Adsorption step was examined by introducing 50mL of 200ppm of each cation solution to the column. The pH of the solution was adjusted by HCl or NaOH. Pb^{+2} , Cd^{+2} , Ni^{+2} , Cu^{+2} and Co^{+2} were examined with dithizone modified adsorbent (SDS/HDZ) where Pb^{+2} , Ni^{+2} , Co^{+2} , Cu^{+2} , Cd^{+2} with PAN modified adsorbent (SDS/PAN) and Ni^{+2} with DMG modified adsorbent (SDS/DMG).

RESULTS AND DISCUSSION

The concentration of SDS was fixed at $7 \times 10^{-3}M$ and below its critical micellization. Negatively charged SDS surfactant ions were adsorbed on the positively charged alumina surface at pH (1-4) (Fig.1). After alumina surfaces were coated with SDS, the ligands; PAN, DMG, HDZ were subsequently immobilized on the SDS coated γ -alumina surface.

Thermal curves of $\gamma-Al_2O_3$, SDS/HDZ, SDS/DMG and SDS/PAN samples are shown in Fig. 2. In TG and

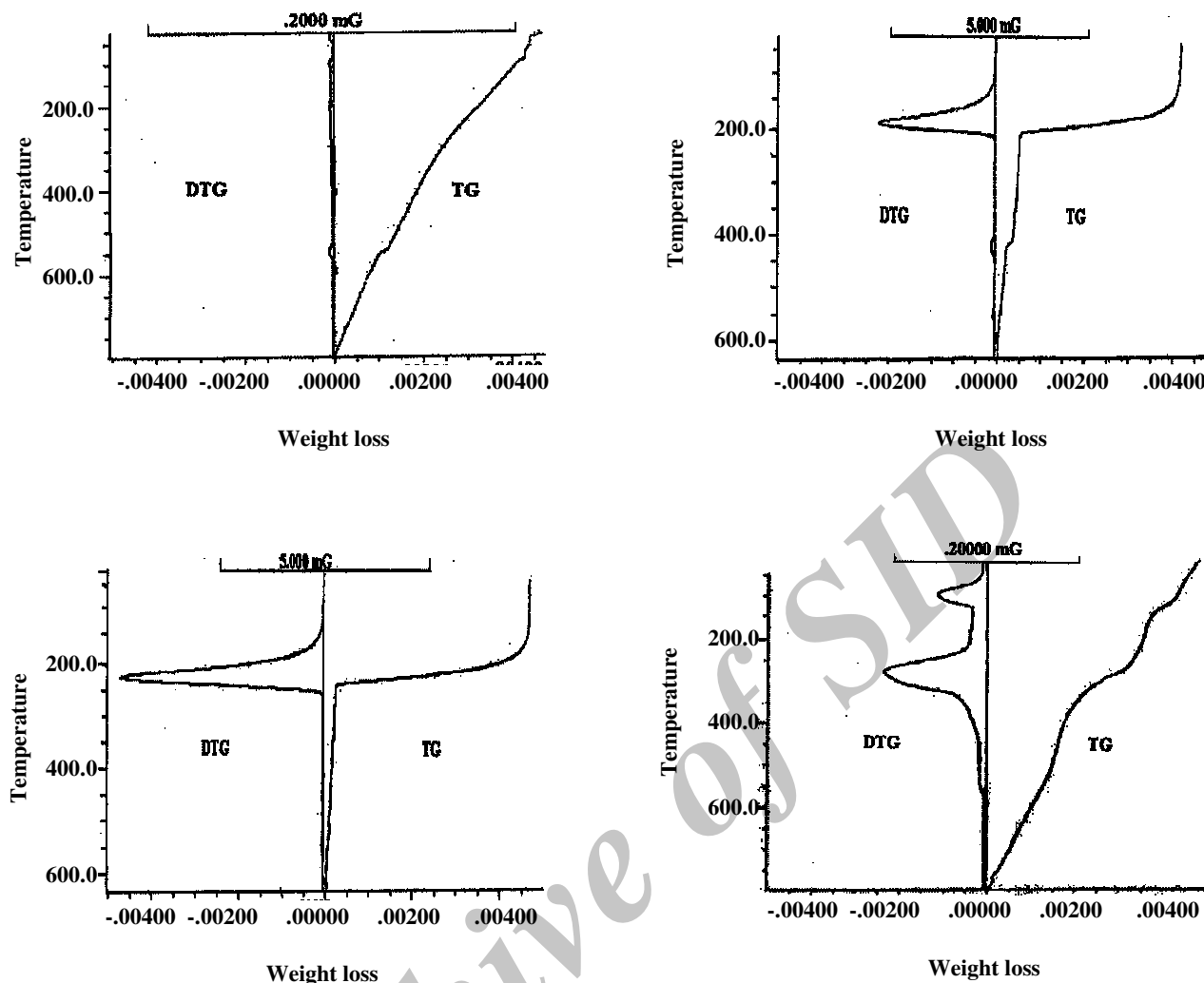


Fig. 2: TG and DTG Curves of $\gamma\text{-Al}_2\text{O}_3$ (a), SDS/HDZ (b), SDS/DMG (c) and SDS/PAN (d).

DTG curves of $\gamma\text{-Al}_2\text{O}_3$ no weight loss peak was observed (Fig. 2-a). The weight loss peaks started from about 175°C and ended at 230°C in SDS/HDZ and SDS/DMG samples indicated that immobilized SDS and the ligands are removed from the surface of alumina (Figs. 2-b and 2-c). In SDS/PAN sample, due to the decomposition of PAN and SDS, two distinct weight loss peaks were respectively observed at 143°C and 230°C (Fig. 2-d).

In the FTIR spectrum of SDS/HDZ, SDS/DMG and SDS/PAN the following characteristic peaks are observed (Fig. 3):

- A strong symmetric stretch peak about 1200 cm^{-1} and a strong unsymmetrical stretch about 1150 cm^{-1} which were assigned to the S=O groups.

- Peaks about 650 cm^{-1} belongs to stretch peak of S-O.

- -CH_3 group bending peak at 1375-1450 cm^{-1} .

These peaks clearly indicated the immobilization of SDS on the alumina surface. In the spectrum of SDS/HDZ (Fig. 3b) a weak band at 1442 cm^{-1} (N=N) and medium band at 1602 cm^{-1} were observed which is assigned to C=C aromatic.

The appearance of the peak at 1277 cm^{-1} is assigned to C=S group showing the immobilization of HDZ onto the alumina surface.

In the FTIR spectrum of SDS/DMG (Fig. 3c) peak observed at 1627 cm^{-1} was assigned to C=N oxime groups. Stretch C-H group of DMG is also appeared at 3248 cm^{-1} .

In the FTIR of SDS/PAN (fig 3d) OH phenolic band and amine ring are appeared around 3200 cm^{-1} . N=N Azo group is observed at 1442 cm^{-1} .

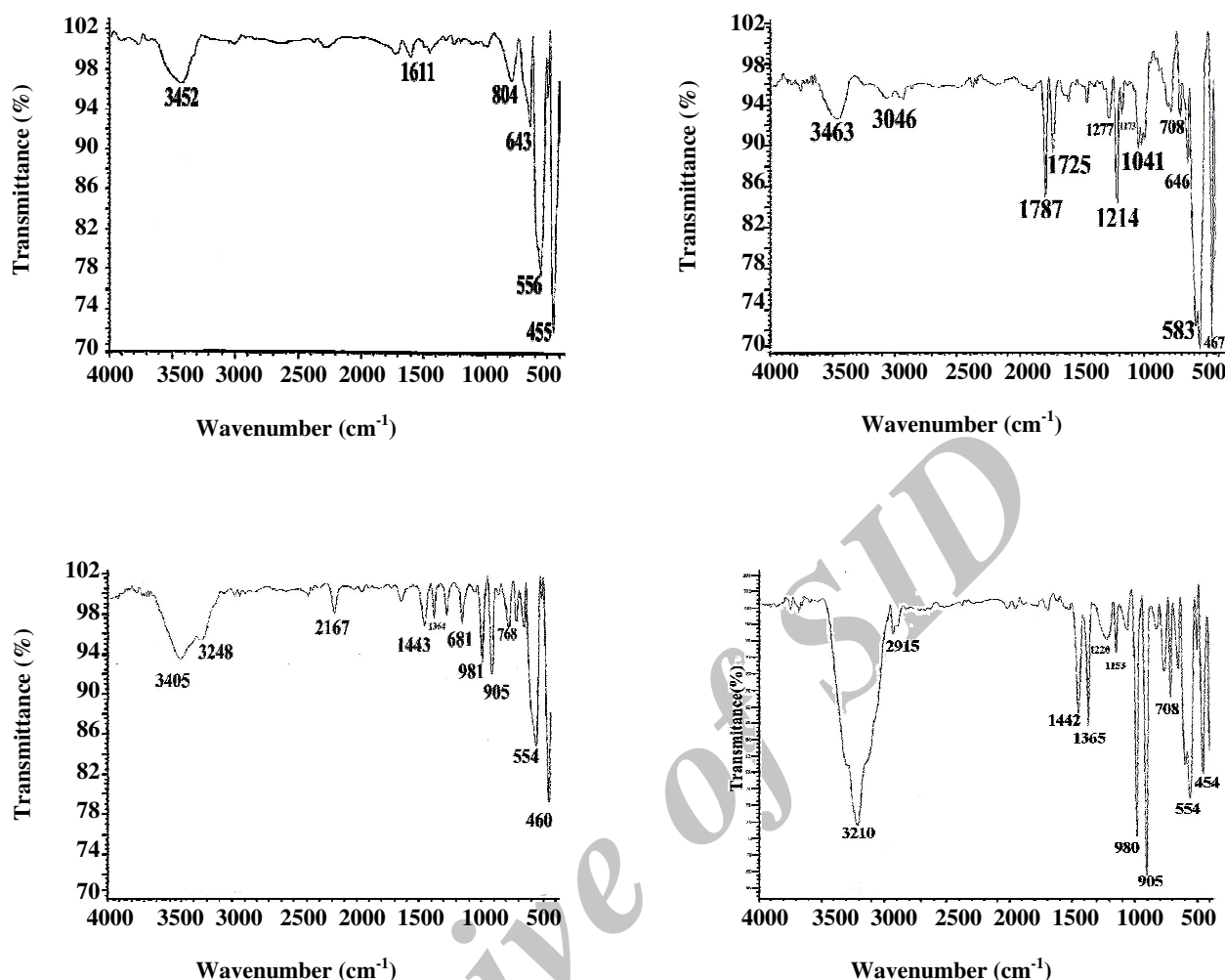


Fig. 3: FTIR on of γ -Al₂O₃ (a), SDS/HDZ (b), SDS/DMG (c) and SDS/PAN (d).

For the adsorption experiments, 50mL of 200ppm solution of Pb²⁺, Cd²⁺, Ni²⁺, Cu²⁺ and Co²⁺ were separately passed through the column packed with SDS/HDZ modified alumina. The pH of the solution was optimized. Under flow rate of 4mL min⁻¹, the cations were retained by the column and were eluted with 10 mL of 4M nitric acid. Quantitative recovery was achieved at pH 1-9 for copper, pH 3-9 for lead and pH 5-9 for cobalt, nickel and cadmium. Therefore, simultaneous removal of the cations can be accomplished in the pH range of 5-9 [12], (Fig. 4).

Adsorption of Pb²⁺, Ni²⁺, Co²⁺, Cu²⁺ and Cd²⁺ by SDS-PAN versus pH is represented in Fig. 5. Quantitative recovery was achieved at pH 1-10 for nickel, pH 3-9 for copper, pH 8-9 for cadmium. Cobalt was quantitatively adsorbed above pH=4. Quantitative adsorption of lead occurred between pH=2-6 (Fig. 5).

The SDS/DMG sample was also used for removal of nickel at different pH (Fig. 6). It was quantitatively retained at pH 7-9. Similar results have been obtained by the other workers obtained by Manzoori [4,13].

Effect of flow rate

The effect of flow rate of the solution on adsorption of Pb²⁺, Ni²⁺, Cd²⁺, Co²⁺, Cu²⁺ by SDS/HDZ sample was studied over range of 1-15mL min⁻¹ (Fig. 7). The adsorption begins to decrease with the increase in the flow rate greater than 10 mL min⁻¹ for copper and cobalt, 7mL min⁻¹ for cadmium and nickel, 14mL min⁻¹ for lead.

The effect of flow rate of the solution on adsorption of Pb²⁺, Ni²⁺, Cd²⁺, Co²⁺, Cu²⁺ by SDS/PAN sample was also studied over range of 1-15mL min⁻¹ (Fig. 8). The adsorption begins to decrease with an increase in the flow

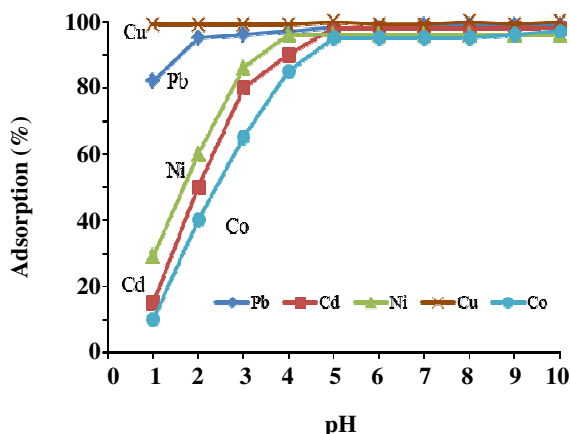


Fig. 4: Effect of pH on the adsorption of cations.

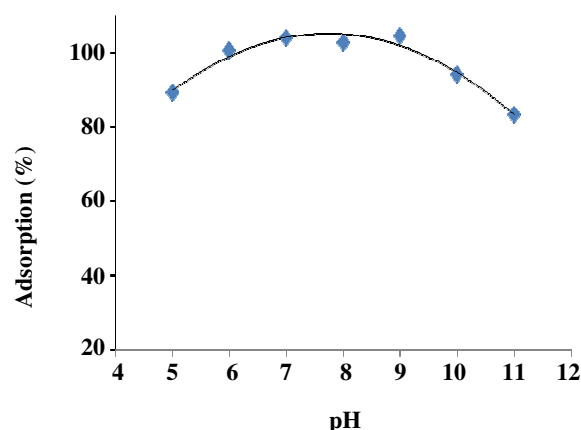


Fig. 6: Effect of pH on adsorption of nickel.

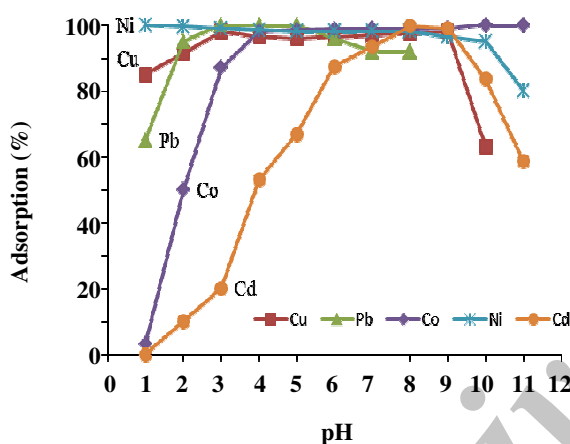


Fig. 5: Effect of pH on the adsorption of cations.

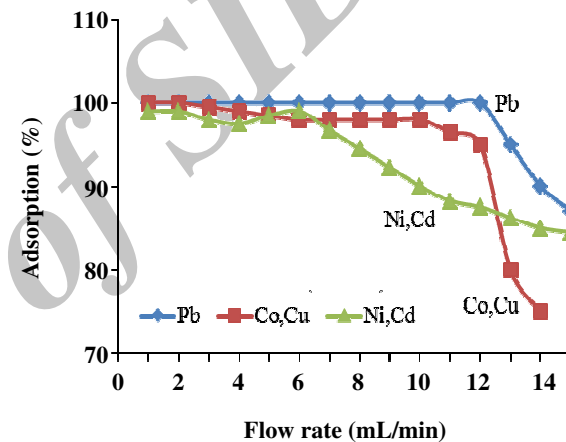


Fig. 7: Effect of flow rate on the adsorption of the cations by (SDS/HDZ).

rate greater than 6 mL min^{-1} for nickel, 5 mL min^{-1} for copper, 4 mL min^{-1} for cadmium, 1 mL min^{-1} for lead and 13 mL min^{-1} for cobalt.

The effect of flow rate of Ni solution on adsorption by SDS/DMG sample was studied over range of $1\text{--}50 \text{ mL min}^{-1}$ (Fig. 9). The adsorption begins to decrease with an increase in the flow rate greater than 20 mL min^{-1} .

Interferences

In order to examine the effects of common coexisting ions on the adsorption of the studied cations, 200ppm solution of each cation containing the added interfering ion was passed through the column. The tolerance of the coexisting ions is considered as the largest amount of that ion which yields a change of less than 5% in the adsorption efficiency. The results showed that between 300 to 1000 times of

the interference ions are tolerable and give less than 5% change in adsorption efficiency, (Tables 1-3).

Application to real sample

The reliability of the presented method was checked by spiking experiments. Three real samples; Zayandehrood water, Isfahan municipal waste water and Karoon water were selected. The recovery of the spiked samples was satisfactorily reasonable (Table 4) and indicating the capability of the method for removal of the cation from complicated matrix.

Reusability of the adsorbent

To test the re-usability of the adsorbents, the SDS/DMG sample was subjected to six adsorption-elution cycles. Several eluents were tested to obtain

Table 1: Effects of some interfering ions on the recovery of the cations by SDS/HDZ sample.

Interfering ions	Interfering* ion/analyte fold ratio	Recovery (%)				
		Pb (II)	Cd (II)	Ni (II)	Cu (II)	Co (II)
Na ⁺	800	98±1	97±1	98±1	93±2	98±1
K ⁺	800	98±1	96±1	95±1	95±1	95±1
Li ⁺	800	97±1	94±1	98±1	93±1	98±1
Ba ²⁺	1000	98±1	98±1	93±1	97±2	93±1
Mg ²⁺	1000	97±1	94±1	96±1	96±1	96±1
Ca ²⁺	1000	97±1	95±1	96±1	97±1	96±1
NH ₄ ⁺	500	96±1	96±1	98±1	94±1	98±1
NO ₃ ⁻	600	96±1	94±1	95±1	97±1	95±1
CH ₃ COO ⁻	300	95±1	95±1	97±1	95±1	97±1
Fe ³⁺	300	96±1	94±1	94±1	96±1	94±1
Cl ⁻	300	96±1	94±1	95±1	95±1	95±1
Tl ⁺	1000	98±1	95±1	96±1	98±1	96±1
Ag ⁺	750	97±1	97±1	98±1	96±1	98±1

*This ratio gives the change of less than 5% in adsorption efficiency of the analyte and is tolerable.

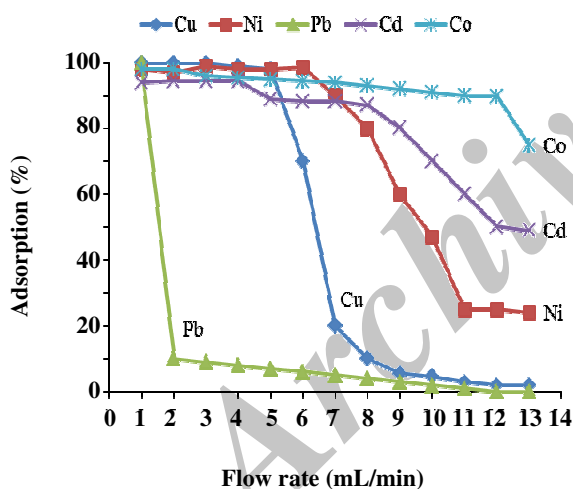


Fig. 8: Effect of flow rate on the adsorption of the cations by SDS/PAN.

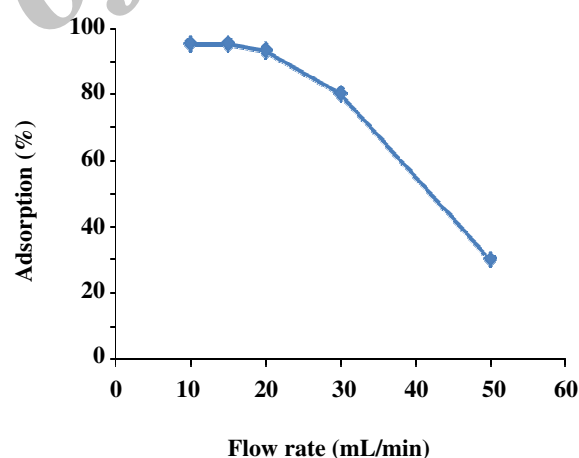


Fig. 9: Effect of flow rate on the adsorption of nickel by SDS/DMG.

the highest recovery and 4M HNO₃ was selected. Adsorption cycles were performed at optimized conditions and the elution operation was carried out by passing 25mL of 4M HNO₃. At the end of each cycle the amount of the cation was measured in the eluted solution. The results showed that Ni²⁺ was perfectly eluted from the adsorbent at the first cycle. It was also observed that after the last cycle

89.8% of the capacity was remained. It can be concluded that the adsorbent can be used repeatedly with satisfactory adsorption capacity (Table 5)

CONCLUSIONS

In the present study, a low cost and environmental friendly solid phase extraction technique was developed

Table 2: Effects of some interfering ions on the recoveries of cations by SDS/PAN sample.

Interfering ions	Interfering* ion/analyte fold ratio	Recovery (%)				
		Cu (II)	Pb (II)	Co (II)	Cd (II)	Ni (II)
Na ⁺	800	96±1	98±1	98±1	94±2	97±1
K ⁺	800	98±1	94±1	98±1	95±1	94±1
Li ⁺	800	98±1	94±1	97±1	93±1	98±1
Ba ²⁺	1000	97±1	96±1	97±1	95±2	95±1
Mg ²⁺	1000	97±1	95±1	98±1	96±1	96±1
Ca ²⁺	1000	97±1	95±1	99±1	94±1	98±1
NH ₄ ⁺	500	98±1	94±1	99±1	94±1	98±1
NO ₃ ⁻	600	96±1	93±1	98±1	94±1	95±1
CH ₃ COO ⁻	300	98±1	98±1	97±1	95±1	97±1
Fe ³⁺	300	97±1	94±1	97±1	96±1	95±1
Cl ⁻	300	96±1	95±1	98±1	97±1	95±1
Tl ⁺	1000	99±1	95±1	98±1	99±1	98±1
Ag ⁺	750	97±1	98±1	97±1	96±1	97±1

*This ratio gives the change of less than 5% in adsorption efficiency of the analyte and is tolerable.

Table 3: Effects of some interfering ions on the recovery of Ni+2 by SDS/DMG sample.

Interfering ions	Interfering* ion/analyte fold ratio	Recovery (%)
		Ni (II)
Na ⁺	800	96±1
K ⁺	800	94±1
Li ⁺	800	98±1
Ba ²⁺	1000	94±1
Mg ²⁺	1000	96±1
Ca ²⁺	1000	98±1
NH ₄ ⁺	500	97±1
NO ₃ ⁻	600	95±1
CH ₃ COO ⁻	300	95±1
Fe ³⁺	300	96±1
Cl ⁻	300	94±1
Tl ⁺	1000	95±1
Ag ⁺	750	96±1

*This ratio gives the change of less than 5% in adsorption efficiency of the analyte and is tolerable.

Table 4: Recovery of the cations from real samples in the presence of interfering ions.

Cation	Sample	¹ added ($\mu\text{g L}^{-1}$)	² Found ($\mu\text{g L}^{-1}$)	Error (%)
Co(II)	Karoon water	20.0	20.4	+2.0
	municipal wastewater	20.0	21.0	+5.0
	Zayandehrood water	20.0	19.6	-2.0
Cd(II)	Karoon water	20.0	19.5	-2.5
	municipal wastewater	20.0	20.3	+1.5
	Zayandehrood water	20.0	19.8	+1.0
Ni(II)	Karoon water	20.0	20.8	+4.0
	municipal waste water	20.0	20.4	+2.0
	Zayandehrood water	20.0	20.1	+0.5
Cu(II)	Karoon water	20.0	19.8	-1.0
	municipal wastewater	20.0	19.6	-2.0
	Zayandehrood water	20.0	20.1	+0.5
Pb(II)	Karoon water	20.0	20.2	+1.0
	municipal wastewater	20.0	19.9	-0.5
	Zayandehrood water	20.0	18.9	-5.5

1-The amount of the spiked cation 2-The measured amount of the spiked cation

Table 5: Reusability of the SDS/DMG sample for Ni^{2+} removal.

Cycles	Recovery (%)
1	100.0
2	98.3
3	97.6
4	95.4
5	93.2
6	89.8

based on immobilization of SDS and ligands onto $\gamma\text{-Al}_2\text{O}_3$. The method can be used for pre-concentration of the studied cations in the presence coexisting ions. It can also be used for simultaneous removal of the cations from the industrial wastewater. The reusability tests applied for SDD/DMG sample showed that 89.8% of the adsorption capacity remained after six cycles. Therefore the adsorbent can be repeatedly used for removal of the studied cations.

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